

## PATENT SPECIFICATION

Application Date : Feb. 4, 1938. No. 3634/38.

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One Complete Specification Left : Jan. 28, 1939.

(Under Section 16 of the Patents and Designs Acts, 1907 to 1938.)

Specification Accepted : Aug. 4, 1939.

## PROVISIONAL SPECIFICATION

No. 3634 A.D. 1938.

## Improvements in and relating to the Production of Coatings on Metal.

WE, THE PYRENE COMPANY LIMITED, a Company organised under the laws of Great Britain, of Great West Road, Brentford, Middlesex, and WILFRED JAMES CLIFFORD and HENRY HEWARD ADAMS, both British Subjects, of the Company's address, do hereby declare the nature of this invention to be as follows:—

10 This invention relates to the production of phosphate and similar coatings on metals in order to improve the resistance of the metals to corrosion, for instance by treating the metals with a solution of  
15 a hydrolysable metal phosphate.

It has now been found that certain compounds containing nitrogen have the property, when added to the coating solutions, of very considerably accelerating the coating operation, in some cases to so great an extent that the coating operation can be carried out in the cold. Among such nitrogen-containing compounds are included organic nitrogen compounds containing oxygen, for instance organic nitro compounds. Examples of suitable nitro compounds are nitro derivatives of aliphatic compounds, such as nitromethane, nitrourea, nitroguanidine and nitourmethane, and nitro derivatives of aromatic compounds, such as nitrobenzene, *m*-, *o*-, or *p*-nitrobenzoic acid and picric acid. Yet another example of a suitable nitrogen compound is hydroxylamine.

The nitrogen-containing compound itself may be added to the coating solution or there may be added a compound which decomposes or reacts in the solution with the formation of the desired nitrogen-containing compound, and in some cases it is also of advantage to add a metallic nitrate. If desired, copper, for instance in the form of copper chloride, may also be added to the solution in order to assist the accelerating action of the nitrogen-containing compound present.

The quantity of nitrogen-containing compound required depends upon the

character of the compound. Thus a suitable concentration is 0.1% when using nitromethane, nitrobenzene, *m*-nitrobenzoic acid or picric acid, 0.2% when using nitroguanidine, and 0.4% when using nitrourea or hydroxylamine.

Certain of the compounds, as indicated above, are capable of accelerating the coating operation to so great an extent that it may be effected in the cold. An example of such a compound is nitroguanidine. Thus a cold solution of manganese phosphate having a normality

$\frac{N}{100}$  of about — free acid (determined by titrating with the aid of methyl orange

indicator) and  $\frac{N}{5}$  total acid (determined by titrating with the aid of phenolphthalein indicator) will not produce a coating on cleaned steel in an hour. The addition of 0.3% of nitroguanidine to such a solution enables a coating to be obtained in 10 minutes.

A further example of the use of nitroguanidine, employing a hot solution, is as follows. A zinc dihydrogen phosphate solution with normality of about  $\frac{n}{20}$  free acid (determined by titrating with the aid of methyl orange indicator) and  $\frac{n}{5}$  total acid (determined by titrating with the aid of phenolphthalein indicator), to which 0.2% of nitroguanidine has been added, will at 80° C. produce an adherent coating on cleaned steel in two minutes. In the absence of the nitroguanidine only a soft non-adherent coating is produced in 10 minutes.

The solutions of the invention may be applied to the metal being coated in any suitable manner, for instance by spraying or immersion methods, and the invention is applicable to coating not only with phosphate solutions, but also to

coating with other solutions which may be employed for improving the resistance of ferrous and other metals to corrosion. Examples of such solutions are those containing the acid radical of an aliphatic dicarboxylic or hydroxy-dicarboxylic acid or of an aromatic carboxylic, phenolic-carboxylic or sul-

phonic acid, e.g. solutions containing oxalic, malonic, tartaric or gallic acid.

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Dated this 4th day of February, 1938.

For the Applicants:

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# PROVISIONAL SPECIFICATION

No. 2901 A.D. 1939.

## Improvements in and relating to the Production of Coatings on Metal

We, THE PYBENE COMPANY LIMITED, a Company organised under the laws of Great Britain, of Great West Road, Brentford, Middlesex, WILFRED JAMES CLIFFORD and HENRY HEWARD ADAMS, both British subjects, and of the Company's address, do hereby declare the nature of this invention to be as follows:—

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This invention relates to the production of phosphate and similar coatings, as defined below, on iron, steel and other metals in order to improve the resistance of the metals to corrosion or to provide a corrosion-resisting base for paints. By coatings similar to phosphate coatings is meant coatings produced with solutions containing the acid radical of an aliphatic dicarboxylic or hydroxy-dicarboxylic acid or of an aromatic carboxylic, phenolic-carboxylic or sulphonic acid, e.g. solutions containing oxalic, malonic, tartaric or gallic acid. The coating solutions may be applied in any suitable manner, for instance by spraying, brushing, flowing or immersion methods.

Certain substances capable of accelerating the production of phosphate and similar coatings on metals are described in British Specification No. 3634/38.

It has now been found that the action of phosphate coating solutions or of the other coating solutions defined above can be accelerated by incorporating in the solution a compound in which there is directly attached to hydrogen or a hydrocarbon residue, which may be substituted or unsubstituted, a non-ionic group which, if substituted into a benzene ring, would have a meta-directing influence to typical electrophilic reagents, i.e. reagents which when caused to react with phenol attack the ortho and para positions preferentially or when caused to react with nitrobenzene attack the meta position preferentially, as for instance do nitric acid and sulphuric acid. By a non-ionic group we mean for the purposes of this specification a

group which neither ionises into two parts in aqueous solution (as for instance do the carboxyl group  $\text{—COOH}$ , the sulphonic acid group  $\text{—SO}_3\text{H}$  and the arsonic acid group  $\text{—AsO}_3\text{H}_2$  and the corresponding salts obtained by replacing ionisable hydrogen in these groups by a cation), nor is a derivative group obtained by modifying the hydroxyl of an acid group (as for instance are the ester group  $\text{—COOCH}_3$  and the acid amide group  $\text{—CONH}_2$ ), whether such derivative group ionises or not. It must be observed that what has been stated above excludes from the present invention the tri- and tetra-alkyl ammonium compounds, for while a group such as  $\text{—NR}_3\text{X}$  (where R is an alkyl group and X an anion) is meta-directing towards electrophilic reagents when substituted in the benzene ring, the compounds in which this group is attached to hydrogen or a hydrocarbon residue R, forming  $\text{HNR}_3\text{X}$  and  $\text{NR}_3\text{X}$  respectively, ionise in aqueous solution by dissociation of the group in question. Similarly the compound  $(\text{CH}_3)_3\text{N}=\text{O}$  is also excluded, for in the presence of water (as in a coating solution) this is converted to the base  $(\text{CH}_3)_3\text{N}(\text{OH})_2$  and the group  $\text{—N}(\text{CH}_3)_2(\text{OH})_2$  ionises with the liberation of hydroxyl. It might be added that where a reference to ionising is made above this is intended to refer to the property of producing an aqueous solution easily detectable concentrations of oppositely charged ions, as for example when a salt or an acid such as acetic or hydrochloric acid is dissolved in water, and not to include infinitesimal, incipient or slow ionisation such as is considered to occur when, for example, tertiary butyl chloride is dissolved in water and undergoes slow hydrolysis by a chemical mechanism believed to involve the slow formation of  $\text{Cl}^-$  and  $(\text{CH}_3)_3\text{C}^+$  ions.

The non-ionic groups included in the invention are such groups as nitro, nitroso, trichlormethyl and aldehyde

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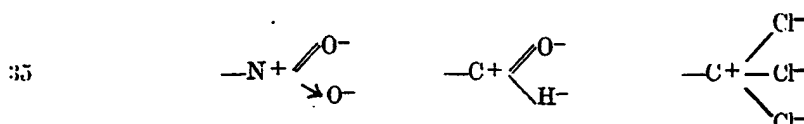
groups. Thus on attempting to introduce further nitro groups into the benzene ring of nitrobenzene, the meta positions in the ring are the most susceptible to attack, as is well known.

By the use of the accelerating compounds of the invention it is possible to reduce the time taken by the coating solution to form a complete coating, or to reduce the temperature, or to obtain a better coating in a given time under given conditions than if the compound were not present.

Certain of the accelerators which may be employed according to the invention contain groups which, although it is believed that they would tend to have a

meta-directing influence on the benzene ring to electrophilic reagents, actually do not readily form phenyl compounds or perhaps form with the phenyl radical compounds which are not sufficiently stable for other substituents to be introduced.

Another definition of compounds which may be employed according to the invention is therefore compounds in which there is directly attached to hydrogen or a hydrocarbon residue a non-ionic group which if it were introduced into a benzene ring would be electron-attracting. Thus in the nitro, aldehyde and trichlormethyl groups the distribution of charges is as follows:—



The positive charges on the nitrogen atom in the case of the nitro group and the carbon atom in each of the other two cases renders these atoms electron-attracting. This electron-attracting quality probably accounts for the meta-directing influence of these groups in the benzene ring.

It might be added here that in principle a decision could be reached in any given case whether a group when introduced into a benzene ring would be electron-attracting or not with respect to the benzene ring, even if in practice the group could not be introduced into the benzene ring without prohibitive experimental difficulty, or, if capable of being introduced into a benzene ring, the compound could not in practice be further substituted successfully.

One of the accelerating groups of the invention is the amine oxide group  $\text{—NH}_2 \text{ O}$ . Incidentally, whilst it is believed that the compound  $\text{C}_6\text{H}_5\text{—NH}_2 \text{ O}$  would tend to substitute in the meta position, in actual fact this tautomerises partly at least to give the form  $\text{C}_6\text{H}_5\text{NHOH}$ , which is ortho-para-directing. Hydroxylamine is an accelerating compound included in the invention, and may be assumed to accelerate owing to its existing partly at least in the amine oxide form.

Where the characteristic or accelerating group is attached to a hydrocarbon residue, the residue may be substituted (in fact all of the hydrogen atoms of the residue may be replaced), but it must of course not contain substituent atoms or groups which destroy the accelerating effect. Thus groups of groups such

as hydroxy, primary-amino and mercapto groups, having the opposite properties of those defined above, i.e. atoms or groups which induce ortho-para substitution to electrophilic reagents or possess an electron-repelling influence in a benzene ring, frequently have a de-accelerating effect, and by substituting into one of the accelerators of the invention sufficient of these de-accelerating groups the accelerating effect may be destroyed. In some cases at least the presence of a single de-accelerating group is not sufficient to destroy the acceleration, for the nitrophenols and nitranilines are accelerators. Again, more than one accelerating group may be attached to the hydrocarbon residue, as in the case of *m*-dinitrobenzene (which contains an accelerating nitro group attached to a nitro-substituted phenol group), and in such cases it would be more difficult to destroy the accelerating effect of the compound by introducing de-accelerating groups. Incidentally, the effect of any given de-accelerating group in a compound depends upon the compound itself, quite apart from the accelerating groups present. Thus although *p*-nitrosophenol is an accelerator and the hydroxy group does not destroy the effect of the nitroso group (although it may reduce it) the compound  $\alpha$ -nitroso- $\beta$ -naphthol is not an accelerator, probably on account of the fact that the additional ring assists the hydroxy group in overcoming the effect of the nitroso group. Moreover, the mononitroresorcinols are accelerators in spite of the fact that they contain two hydroxy groups.

Certain of the accelerating compounds of the invention are liable to become

decomposed in the course of the coating with the production of de-accelerating compounds. Such is the case with nitrobenzene, for instance, which is liable to be reduced by the hydrogen liberated in the coating process with the production of aniline, a de-accelerating compound on account of the presence of the ortho-para-directing amino group. This is theoretically a disadvantage with all nitro groups, which tend to reduce to amino groups. If the accumulation of the de-accelerating compound becomes serious, the disadvantage can sometimes be overcome by incorporating a nitrate in the coating solution. In some cases the nitrate is reduced to nitrite and the nitrite reacts with the amine to form a volatile hydroxy-compound which escapes from the solution. In some cases, again, the reduction products of the nitro compound are not deleterious. Thus nitroguanidine on reduction yields ammonia and carbon dioxide, and nitromethane yields methylamine, which for some reason has little or no de-accelerating effect.

Examples of the accelerating compounds defined in the preceding paragraphs are nitromethane, nitrobenzene, *o*-, *m*- and *p*-nitrophenols, *o*-, *m*- and *p*-nitranilines, *o*-, *m*- and *p*-nitrobenzoic acids and picric acid, in which the accelerating group is the nitro group, *p*-nitrosophenol and *p*-nitrosodimethylaniline, in which the accelerating group is the nitroso group, hydroxylamine, in which the accelerating group is the amine oxide group (for hydroxylamine reacts partly at least in the form  $\text{H.NH}_2=\text{O}$ ), formaldehyde (introduced in the form of paraformaldehyde, for example) and benzaldehyde, in which the accelerating group is the aldehyde group, and trichloroacetic acid, in which the accelerating group is the trichloromethyl group, and this is attached to a methyl group substituted by an oxygen atom and a hydroxyl group to give the grouping  $-\text{C}(\text{OH})=\text{O}$ . Other

examples are esters of trichloroacetic acid, e.g. ethyl trichloroacetate. Yet another example is chloral,  $\text{CCl}_3\text{CHO}$ , which may be regarded as a trichloromethyl group attached to a methyl group substituted to give the aldehyde grouping  $-\text{CHO}$ , or an aldehyde group attached to a trichloromethyl group, and thus falls into two of the above classes.

In general, the accelerating compound may if desired be introduced into the coating solution by the addition of a substance which decomposes or reacts in the solution with the formation of the desired accelerating compound.

In the compounds defined above containing a hydrocarbon residue, substituted or unsubstituted, and an accelerating group the group is attached directly to the residue. It has been found that compounds in which the accelerating group is attached to the residue not directly but through the agency of a single nitrogen atom have an accelerating effect also, and the above remarks on the presence of de-accelerating groups apply here also. In general the structure of these accelerating compounds will be of the type  $\text{R.NH.X}$ , where R is the substituted or unsubstituted hydrocarbon residue and X is a nitro or other accelerating group, although the hydrogen atom attached to the nitrogen may itself be substituted, for instance by a methyl or other alkyl group. Examples of the accelerating compounds referred to in this paragraph

are nitrourea  $\text{CO} \begin{matrix} \text{NH.NO}_2 \\ \text{NH}_2 \end{matrix}$ , in which

the accelerating group is the nitro group and the hydrocarbon residue  $\text{CH}_3-$  contains as substituents an oxygen atom and an amino group, nitroguanidine

$\text{NH}=\text{C} \begin{matrix} \text{NH.NO}_2 \\ \text{NH}_2 \end{matrix}$ , which is a similar

compound in which an  $\text{NH}=\text{}$  group is present instead of the oxygen atom, and nitro-urethane  $\text{C}_2\text{H}_5\text{OOC.NH.NO}_2$  and nitroso-N-methylurethane  $\text{C}_2\text{H}_5\text{OOC.N}(\text{CH}_3).\text{NO}$ , in which the ester grouping  $\text{C}_2\text{H}_5\text{O}-$  is substituted into the hydrocarbon residue  $\text{CH}_3-$ .

The optimum concentration of the accelerating compound in the coating solution differs with different compounds, but in the case of phosphate coating solutions is in general from about 0.01% to 0.4% by weight of the solution. Too much or too little of the accelerating compound may be detrimental to good results. Furthermore, even at optimum concentrations all compounds do not give the same accelerating effect. It appears probable in many cases that with a given accelerating group the smaller the molecule the more efficient the accelerating action at optimum concentration, while in the case of de-accelerating groups the smaller the molecule the less the de-accelerating action, but this is by no means certain. The optimum concentrations and efficiencies at optimum concentration of various compounds which may be employed according to the invention are given in the following table, the results being arrived at by adding the compound to a solution of zinc dihydrogen phosphate having a normality

$\frac{N}{20}$  of — free acid (determined by titrating with the aid of methyl orange indicator)  
 $\frac{N}{5}$  and — total acid (determined by titrating with the aid of phenol-phthalein

indicator) and treating a cleaned steel sheet for 2 minutes at 80° C. The cleaned steel sheet referred to here and in the examples given below is a steel sheet in its original bright rolled condition rendered substantially free from grease by wiping with clean white spirit.

	Substance.	Optimum Concentration.	Efficiency.
	Picric acid	0.1%	Very Good
15	Nitroguanidine	0.2%	" "
	Hydroxylamine	0.3%	" "
	Trichloroacetic acid	0.05%	" "
	Nitrobenzene	0.1%	" Good
	Nitromethane	0.1%	" "
20	Nitrourethane	0.2%	" "
	Nitroso-N-methylurethane	0.2%	" "
	<i>o</i> -Nitraniline	0.05%	" "
	<i>m</i> - or <i>p</i> -Nitraniline	0.04%	" "
	<i>m</i> - or <i>p</i> -Nitrophenol	0.04%	" "
25	<i>p</i> -nitroso-dimethylaniline	0.04%	" "
	Nitrourea	0.4%	Slight acceleration
	<i>m</i> -Nitrobenzoic acid	0.1%	" "
	<i>o</i> -Nitrophenol	0.1%	" "
	Benzaldehyde	0.2%	Very slight acceleration
30	Paraformaldehyde	0.2%	" " "
	<i>p</i> -Nitrosophenol	0.4%	" " "
	Chloral	0.2%	" " "

While the compounds of the invention may be the only accelerators present in the coating bath, they may also be employed in conjunction with other accelerators, for instance metallic accelerators such as copper compounds, or oxidising agent accelerators such as nitrates or nitrites. The presence of copper ions appears to promote heavier and darker coatings, and the presence of a nitrate such as zinc nitrate appears to give a slight further acceleration. The invention is illustrated by the following examples:—

#### EXAMPLE 1.

A cleaned steel sheet can be successfully coated with a phosphate coating by treating it at a temperature of from 15 to 80° C. with a solution of zinc or manganese dihydrogen phosphate, of concentration  $\frac{N}{5}$  when determined using phenol-phthalein as indicator, containing 0.05% of nitroguanidine.

#### EXAMPLE 2.

A cleaned steel sheet can be successfully coated by treating it with an  $\frac{N}{5}$

solution of zinc dihydrogen phosphate (determined by phenol-phthalein) containing 0.4% of hydroxylamine, at a temperature of 80° C.

#### EXAMPLE 3.

A clean steel sheet can be successfully coated by treating it at a temperature of

15° to 80° C. with an  $\frac{N}{5}$  solution of manganese dihydrogen phosphate (determined by phenol-phthalein) containing 0.1% hydroxylamine.

If in any of the above examples 0.001% of copper (calculated as the metal) is added to the solution, for instance in the form of the nitrate or carbonate, a darker and slightly heavier coating is obtained, and the addition of zinc nitrate results in a slight further acceleration.

Dated this 27th day of January, 1939.

For the Applicants:

GILL, JENNINGS & EVERY,  
 Chartered Patent Agents,  
 51/52, Chancery Lane, London, W.C.2.

## COMPLETE SPECIFICATION

## Improvements in and relating to the Production of Coatings on Metal.

We, THE PYRENE COMPANY LIMITED, a Company organised under the laws of Great Britain, of Great West Road, Brentford, Middlesex, WILFRED JAMES CLIFFORD and HENRY HEWARD ADAMS, both British subjects, and of the Company's address, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of phosphate and similar coatings, as defined below, on iron, steel and other metals in order to improve the resistance of the metals to corrosion or to provide a corrosion-resisting base for paints. By coatings similar to phosphate coatings is meant coatings produced with solutions containing the acid radical of an aliphatic dicarboxylic or hydroxy-dicarboxylic acid or of an aromatic carboxylic, phenolic-carboxylic or sulphonic acid, e.g. solutions containing oxalic, malonic, tartaric or gallic acid. The coating solutions may be applied in any suitable manner, for instance by spraying, brushing, flowing or immersion methods.

According to the invention, the action of phosphate coating solutions or of the other coating solutions defined above is accelerated by incorporating in the solution a compound in which there is directly attached to hydrogen or a hydrocarbon residue, which may be substituted or unsubstituted, a non-ionic group (other than a cyanide or isocyanide group) which, if substituted into a benzene ring, would have a meta-directing influence to typical electrophilic reagents, i.e. reagents which when caused to react with phenol attack the ortho and para positions preferentially or when caused to react with nitrobenzene attack the meta position preferentially, as for instance do nitric acid and sulphuric acid. By a non-ionic group we mean for the purposes of this specification a group which neither ionises into two parts in aqueous solution (as for instance do the carboxyl group  $\text{—COOH}$ , the sulphonic acid group  $\text{—SO}_3\text{H}$  and the arsonic acid group  $\text{—AsO}_3\text{H}_2$ , and the corresponding salts obtained by replacing ionisable hydrogen in these groups by a cation), nor is a derivative group obtained by modifying the hydroxyl of an acid group (as for instance are the ester group  $\text{—COOCH}_3$  and the acid amide group

$\text{—CONH}_2$ ), whether such derivative group ionises or not. It must be observed that what has been stated above excludes from the present invention the tri- and tetra-alkyl ammonium compounds, for while a group such as  $\text{—NR}_3\text{X}$  (where R is an alkyl group and X an anion) is meta-directing towards electrophilic reagents when substituted in the benzene ring, the compounds in which this group is attached to hydrogen or a hydrocarbon residue R, forming  $\text{HNR}_3\text{X}$  and  $\text{NR}_3\text{X}$  respectively, ionise in aqueous solution by dissociation of the group in question. Similarly the compound  $(\text{CH}_3)_3\text{N}=\text{O}$  is also excluded, for in the presence of water (as in a coating solution) this is converted to the base  $(\text{CH}_3)_3\text{N}(\text{OH})_2$ , and the group  $\text{—N}(\text{CH}_3)_2(\text{OH})_2$  ionises with the liberation of hydroxyl. It might be added that where a reference to ionising is made above this is intended to refer to the property of producing in aqueous solution easily detectable concentrations of oppositely charged ions, as for example when a salt or an acid such as acetic or hydrochloric acid is dissolved in water, and not to include infinitesimal, incipient or slow ionisation such as is considered to occur when, for example, tertiary butyl chloride is dissolved in water and undergoes slow hydrolysis by a chemical mechanism believed to involve the slow formation of  $\text{Cl}^-$  and  $(\text{CH}_3)_3\text{C}^+$  ions.

The non-ionic groups included in the invention are such groups as nitro, nitroso, trichloromethyl and aldehyde groups. Thus on attempting to introduce further nitro groups into the benzene ring of nitrobenzene, the meta positions in the ring are the most susceptible to attack, as is well known.

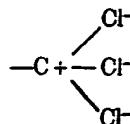
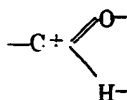
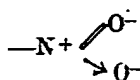
By the use of the accelerating compounds of the invention it is possible to reduce the time taken by the coating solution to form a complete coating, or to reduce the temperature, or to obtain a better coating in a given time under given conditions than if the compound were not present.

Certain of the accelerators which may be employed according to the invention contain groups which, although it is believed that they would tend to have a meta-directing influence in the benzene ring to electrophilic reagents, actually do not readily form phenyl compounds or perhaps form with the phenyl radical compounds which are not sufficiently stable for other substituents to be intro-

duced.

Another definition of compounds which may be employed according to the invention is therefore compounds in which there is directly attached to hydrogen or a hydrocarbon residue a non-ionic group

(other than a cyano or isocyanide group) which if it were introduced into a benzene ring would be electron-attracting. Thus in the nitro, aldehyde and trichloromethyl groups the distribution of charges is as follows:—



The positive charges on the nitrogen atom in the case of the nitro group and the carbon atom in each of the other two cases renders these atoms electron-attracting. This electron-attracting quality probably accounts for the meta-directing influence of these groups in the benzene ring.

It might be added here that in principle a decision could be reached in any given case whether a group when introduced into a benzene ring would be electron-attracting or not with respect to the benzene ring, even if in practice the group could not be introduced into the benzene ring without prohibitive experimental difficulty, or, if capable of being introduced into a benzene ring, the compound could not in practice be further substituted successfully.

One of the accelerating groups of the invention is the amine oxide group  $-\text{NH}_2=\text{O}$ . Incidentally, while it is believed that the compound  $\text{C}_6\text{H}_5-\text{NH}_2=\text{O}$  would tend to substitute in the meta position, in actual fact this tautomerises partly at least to give the form  $\text{C}_6\text{H}_5\text{NH.OH}$ , which is ortho-para-directing. Hydroxylamine is an accelerating compound included in the invention, and may be assumed to accelerate owing to its existing partly at least in the amine oxide form.

Where the characteristic or accelerating group is attached to a hydrocarbon residue, the residue may be substituted (in fact all of the hydrogen atoms of the residue may be replaced), but it must of course not contain substituent atoms or groups which destroy the accelerating effect. Thus atoms, or groups such as hydroxy, primary-amino and mercapto groups, having the opposite properties of those defined above, i.e. atoms or groups which induce ortho-para substitution to electrophilic reagents or possess an electron-repelling influence in a benzene ring, frequently have a de-accelerating effect, and by substituting into one of the accelerators of the invention sufficient of these de-accelerating groups the accelerating effect may be destroyed. In some cases at

least the presence of a single de-accelerating group is not sufficient to destroy the acceleration, for the nitrophenols and nitranilines are accelerators. Again, more than one accelerating group may be attached to the hydrocarbon residue, as in the case of *m*-dinitrobenzene (which contains an accelerating nitro group attached to a nitro-substituted phenyl group), and in such cases it would be more difficult to destroy the accelerating effect of the compound by introducing de-accelerating groups. Incidentally, the effect of any given de-accelerating group in a compound depends upon the compound itself, quite apart from the accelerating groups present.

Thus although *p*-nitrosophenol is an accelerator and the hydroxy group does not destroy the effect of the nitroso group (although it may reduce it) the compound *o*-nitroso- $\beta$ -naphthol is not an accelerator, probably on account of the fact that the additional ring assists the hydroxy group in overcoming the effect of the nitroso group. Moreover, the mononitroresorcinols are accelerators in spite of the fact that they contain two hydroxy groups.

Certain of the accelerating compounds of the invention are liable to become decomposed in the course of the coating with the production of de-accelerating compounds. Such is the case with nitrobenzene, for instance, which is liable to be reduced by the hydrogen liberated in the coating process with the production of aniline, a de-accelerating compound on account of the presence of the ortho-para-directing amino group. This is theoretically a disadvantage with all nitro groups, which tend to reduce to amino groups. If the accumulation of the de-accelerating compound becomes serious, the disadvantage can sometimes be overcome by incorporating a nitrate in the coating solution. In some cases the nitrate is reduced to nitrite and the nitrite reacts with the amine to form a volatile hydroxy-compound which escapes from the solution. In some cases, again, the reduction products of the nitro compound are not deleterious. Thus nitroguanidine on reduction yields

ammonia and carbon dioxide, and nitromethane yields methylamine, which for some reason has little or no de-accelerating effect.

- 5 Examples of the accelerating compounds defined in the preceding paragraphs are nitromethane, nitrobenzene, *o*-, *m*- and *p*-nitrophenols, *o*-, *m*- and *p*-nitranilines, *o*-, *m*- and *p*-nitrobenzoic acids and picric acid, in which the accelerating group is the nitro group, *p*-nitrosophenol and *p*-nitrosodimethylaniline, in which the accelerating group is the nitroso group, hydroxylamine, in which the accelerating group is the amine oxide group (for hydroxylamine reacts partly at least in the form  $\text{H.NH}_2=\text{O}$ ), formaldehyde (introduced in the form of paraformaldehyde, for example) and benzaldehyde, in which the accelerating group is the aldehyde group, and trichloroacetic acid, in which the accelerating group is the trichlormethyl group, and this is attached to a methyl group substituted by an oxygen atom and a hydroxyl group to

give the grouping  $\text{—C} \begin{array}{l} \text{O} \\ \text{OH} \end{array}$  Other

- examples are esters of trichloroacetic acid, e.g. ethyl trichloroacetate. Yet another example is chloral,  $\text{CCl}_3\text{CHO}$ , which may be regarded as a trichlormethyl group attached to a methyl group substituted to give the aldehyde grouping  $\text{—CHO}$ , or an aldehyde group attached to a trichlormethyl group, and thus falls into two of the above classes.

- 35 In general, the accelerating compound may if desired be introduced into the coating solution by the addition of a substance which decomposes or reacts in the solution with the formation of the desired accelerating compound.

- 40 In the compounds defined above containing a hydrocarbon residue, substituted or unsubstituted, and an accelerating group the group is attached directly to the residue. It has been found that compounds in which the accelerating group is attached to the residue not directly but through the agency of a single nitrogen atom have an accelerating effect also, and the above remarks on the presence of de-accelerating groups apply here also. In general the structure of these accelerating compounds will be of the type  $\text{R.NH.X}$ , where R is the substituted or unsubstituted hydrocarbon residue and X is a nitro or other accelerating group, although the hydrogen atom attached to the nitrogen may itself be substituted,

for instance by a methyl or other alkyl group. Examples of the accelerating compounds referred to in this paragraph

are nitrourea  $\text{CO} \begin{array}{l} \text{NH.NO}_2 \\ \text{NH}_2 \end{array}$ , in which

the accelerating group is the nitro group and the hydrocarbon residue  $\text{CH}_3\text{—}$  contains as substituents an oxygen atom and an amino group, nitroguanidine

$\text{NH}=\text{C} \begin{array}{l} \text{NH.NO}_2 \\ \text{NH}_2 \end{array}$ , which is a similar

compound in which an  $\text{NH=}$  group is present instead of the oxygen atom, and nitro-urethane  $\text{C}_2\text{H}_5\text{OOC.NH.NO}_2$  and nitroso-N-methylurethane  $\text{C}_2\text{H}_5\text{OOC.N(CH}_3\text{).NO}$ .

in which the ester group  $\text{C}_2\text{H}_5\text{O} \begin{array}{l} \text{O} \\ \text{O} \end{array}$  is substituted into the hydrocarbon residue  $\text{CH}_3\text{—}$ .

The optimum concentration of the accelerating compound in the coating solution differs with different compounds, but in the case of phosphate coating solutions is in general from about 0.01% to 0.4% by weight of the solution. Too much or too little of the accelerating compound may be detrimental to good results. Furthermore, even at optimum concentrations all compounds do not give the same accelerating effect. It appears probable in many cases that with a given accelerating group the smaller the molecule the more efficient the accelerating action at optimum concentration, while in the case of de-accelerating groups the smaller the molecule the less the de-accelerating action, but this is by no means certain. The optimum concentrations and efficiencies at optimum concentration of various compounds which may be employed according to the invention are given in the following table, the results being arrived at by adding the compound to a solution of zinc dihydrogen phosphate having a normality

N of — free acid (determined by titrating with the aid of methyl orange indicator)

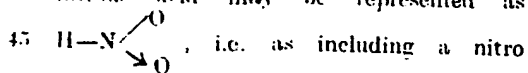
N and — total acid (determined by titrating with the aid of phenolphthalein indicator) and treating a cleaned steel sheet for 2 minutes at 80° C. The cleaned steel sheet referred to here and in the examples given below is a steel sheet in its original bright rolled condition rendered substantially free from grease by wiping with clean white spirit.

105 110



Substance.	Optimum Concentration.	Efficiency.
Picric acid	0.1%	Very Good
Nitroguanidine	0.2%	" "
5 Hydroxylamine	0.3%	" "
Trichloroacetic acid	0.05%	" "
Nitrobenzene	0.1%	" "
Nitromethane	0.1%	Good
Nitrourethane	0.2%	" "
10 Nitroso-N-methylurethane	0.2%	" "
o-Nitraniline	0.05%	" "
m- or p-Nitraniline	0.04%	" "
m- or p-Nitrophenol	0.04%	" "
p-nitroso-dimethylaniline	0.04%	" "
15 Nitrourea	0.4%	" "
m-Nitrobenzoic acid	0.1%	Slight acceleration
o-Nitrophenol	0.1%	" "
Benzaldehyde	0.2%	" "
Paraformaldehyde	0.2%	Very slight acceleration
20 p-Nitrosophenol	0.4%	" "
Chloral	0.2%	" "

While the compounds of the invention may be the only accelerators present in the coating bath, they may also be employed in conjunction with other accelerators, for instance metallic accelerators such as copper compounds, or oxidising agent accelerators such as nitrates or nitrites. The presence of copper ions appears to promote heavier and darker coatings, and the presence of a nitrate such as zinc nitrate appears to give a slight further acceleration. It should be added here that the normal formula for nitrous acid is  $\text{H}-\text{O}-\text{N}=\text{O}$  in which hydrogen is attached to the nitrite group  $-\text{O}-\text{N}=\text{O}$ , and this does not fall within the definitions of accelerating compounds given earlier in this specification, for in the benzene ring the nitrite group is not meta-directing to electrophilic reagents, and is not electron-attracting. However, as the formula of nitrous acid may be represented as



group, we wish to make it clear that we do not include in the claims the use of nitrous acid as the said accelerating compound, although nitrous acid may be present in addition to the said compound, as will be clear from the above reference to the use of nitrites in addition to the accelerating compounds of the invention.

50 Certain of the accelerating compounds of the invention are so effective that coatings can be produced from phosphate solutions containing them in the cold, as is the case with nitroguanidine.

55 The invention is illustrated by the following examples:—

#### EXAMPLE 1.

This is an example of the use of nitroguanidine to accelerate a coating operation to so great an extent that it can be effected in the cold.

65 A cold solution of manganese phosphate having a normality of about —

free acid (determined by titrating with the aid of methyl orange indicator) and

— total acid (determined by titrating

with the aid of phenol-phthalein indicator) will not produce a coating on a cleaned steel sheet in an hour. The addition of 0.3% of nitroguanidine to such a solution enables a coating to be obtained in 10 minutes.

#### EXAMPLE 2.

This is an example of the use of nitroguanidine in a hot solution.

70 A zinc dihydrogen phosphate solution with normality of about — free acid

(determined by titrating with the aid of methyl orange indicator) and — total

acid (determined by titrating with the aid of phenol-phthalein indicator), to which 0.2% of nitroguanidine has been added, will at 80° C. produce an adherent coating on a cleaned steel sheet in two minutes. In the absence of the nitroguanidine only a soft non-adherent coating is produced in 10 minutes.

#### EXAMPLE 3.

80 A cleaned steel sheet can be success-

fully coated with a phosphate coating by treating it at a temperature of from 15 to 80° C. with a solution of zinc or manganese dihydrogen phosphate, of

- 5 concentration — when determined using  
5 phenol-phthalein as indicator, containing 0.05% of nitroguanidine.

EXAMPLE 4.

- A cleaned steel sheet can be success-  
10 fully coated by treating it with an —  
5 solution of zinc dihydrogen phosphate (determined by phenol-phthalein) containing 0.4% of hydroxylamine, at a temperature of 80° C.

15 EXAMPLE 5.

- A cleaned steel sheet can be success-  
fully coated by treating it at a tempera-  
N ture of 15° to 80° C. with an — solution  
5 of manganese dihydrogen phosphate (determined by phenol-phthalein) containing 0.4% hydroxylamine.

- If in any of the above examples  
0.001% of copper (calculated as the  
25 metal) is added to the solution, for instance in the form of the nitrate or carbonate, a darker and slightly heavier coating is obtained, and the addition of zinc nitrate results in a slight further acceleration.

- 30 Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

- 35 1. A process for improving the resistance of metal to corrosion by treating the metal with a phosphate coating solution, in which the action of the solution is accelerated by means of an accelerating  
40 compound in which there is directly attached to hydrogen or a hydrocarbon residue a non-ionic group (other than a cyanide or isocyanide group) which, if substituted into a benzene ring, would  
45 have a meta-directing influence to typical electrophilic reagents.

2. A process for improving the resistance of metal to corrosion by treating the metal with a phosphate coating solution, in which the action of the solution  
50 is accelerated by means of an accelerating compound in which there is directly attached to hydrogen or a hydrocarbon residue a non-ionic group (other than a  
55 cyanide or isocyanide group) which if it were introduced into a benzene ring would be electron-attracting.

3. A modification of the process of Claim 1 or 2, in which the said group

is attached to a hydrocarbon residue not directly but through the agency of a single nitrogen atom.

4. A process for improving the resistance of metal to corrosion by treating the metal with a phosphate coating solution, in which the action of the solution is accelerated by means of an accelerating compound in which a nitro group is attached to a hydrocarbon residue directly or through the agency of a single  
70 nitrogen atom.

5. A process for improving the resistance of metal to corrosion by treating the metal with a phosphate coating solution, in which the action of the solution is accelerated by means of an accelerating compound in which a nitroso, amine oxide, trichlormethyl or aldehyde group is attached to a hydrocarbon residue directly or through the agency of a  
80 single nitrogen atom.

6. A process according to any of the preceding claims, in which the hydrocarbon residue is unsubstituted.

7. A process according to any of Claims 1 to 5, in which the hydrocarbon residue is substituted.

8. A process for improving the resistance of metal to corrosion by treating the metal with a phosphate coating solution, in which the action of the solution is accelerated by means of hydroxyl-  
90 amine.

9. A process according to Claim 4, in which the said compound is nitro-  
95 methane, nitrobenzene, or picric acid.

10. A process according to Claim 4, in which the said compound is a nitraniline, a nitrophenol, a nitrobenzoic acid or a nitroresorcinol.

11. A process according to Claim 4, in which the said compound is nitrourea or nitrourethane.

12. A process according to Claim 4, in which the said compound is nitro-  
100 guanidine.

13. A process according to Claim 5, in which the said compound is formaldehyde, chloral, benzaldehyde, *p*-nitrosophenol, *p*-nitroso-dimethylaniline or nitroso-N-  
110 methylurethane.

14. A process according to Claim 5, in which the said compound is trichloroacetic acid or an ester thereof.

15. A process according to any of the preceding claims, in which a nitrate, nitrite or other oxidising agent accelerator is present in addition to the said accelerating compound.

16. A process according to any of the preceding claims, in which a copper compound or other metallic accelerator is present in the coating solution.

17. A process according to any of the

preceding claims, added to the coating of iron or steel.

19. A modification of the process of any of the preceding claims, in which the coating solution is not a phosphate solution but a solution containing the acid radical of an aliphatic dicarboxylic or hydroxy-dicarboxylic acid or of an aromatic carboxylic, phenolic-carboxylic or sulphonc acid.

19. A process substantially as de-

scribed with reference to any one of the Examples.

20. Metal which has been rendered of improved resistance to corrosion by any of the processes of the preceding claims. 15

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